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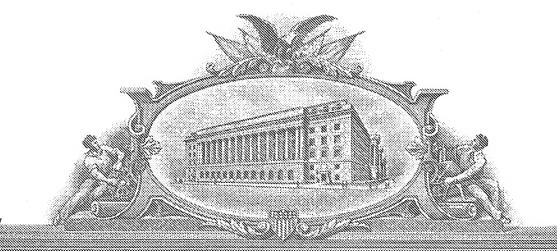
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This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53 (c).

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Additional inventors are being named on the 1 separately numbered sheets attached hereto								
TITLE OF THE INVENTION (500 characters max)								
METHOD AND APPARATUS FOR HIGH SELECTIVITY SILICON NITRIDE ETCHING								
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Applicant claims small entity status. See 37 CFR 1.27.								
A check or money order is enclosed to cover the filing fees FILING FEE Amount (\$):								
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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.								
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Docket Number 108430.040 INVENTOR(S)/APPLICANT(S)						
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Patent Disclosure CONFIDENTIAL

METHOD AND APPARATUS FOR HIGH SELECTIVITY SILICON NITRIDE ETCHING

Ismail Kashkoush, Gim Chen and Rich Novak

December 21, 2003



Patent Disclosure CONFIDENTIAL

OBJECTIVE

To develop a process that yields a high selectivity silicon nitride (Si_3N_4) to silicon oxide (SiO_2) etch rates in IC manufacturing. The process of etching Si_3N_4 in phos acid is commonly used in IC manufacturing because of its stable etch rate. However, the selectivity suffers i.e. increases over the bath life. The number of wafers processed in the bath influence the selectivity. Etch byproducts suppress the oxide etch rate.

MATERIAL AND EXPERIMENTAL SETUP

An acid bath was used to etch SN wafers. The bath is filtered, heated and filtered. Process conditions were: Sulfuric:Phos:water

Temp. 165 C

Rinse: 3 QDR + 10 min. cascade

Concentration control to maintain the mix ration throughout the bath

Feed and bleed may be required

- •200mm nitride wafers and thermal oxide wafers were used.
- •System configured with recirculated PRM and N₂ sparging
- •Bath temperature = 165 deg. C
- •Prior to testing, wafers were run through dilute HF for surface normalization.
- •Test wafers from different sources were run together and showed slightly different etch rates. The average was used.
- •Etch rate measurement was performed using Rudolph S300 with 49 point measurements in 5mm edge exclusion.
- •Nitride loading effects were tested by processing full lots of nitride wafers for an extended period of time.

Methods of Control

- a. Concentration sensor e.g. NIR, FT-NIR: the system will monitor the concentration of sulfuric acid, phosphoric acid and water. The user will select the setpoint and the system will maintain the setpoint by injecting the right constituent to adjust. For example, the system will inject sulfuric acid if it goes lower than the specified value.
- b. Feed and bleed: to reduce the effect of the etch by products, a supply of chemicals will be activated. The user will program the frequency and volumes.

RESULTS AND DISCUSSION

Figure 1 shows the test apparatus where the acid mix flows from to process tank thru a concentration sensor, the pump, the heater, filters, and then back to the process tank.. The mix of chemicals is initially dispensed from the dispense lines according to the desired mix ratio. The process controller constantly monitors the chemicals concentrations and adjusts accordingly from the spike lines by opening and closing the control valves.

Figure 2 shows the etch rate (ER) of silicon nitride to silicon dioxide over time. As the data show, the selectivity obtained (ER of Si3N4 / ER of SiO2) was higher that traditional nitride etch in phosphoric acid. Typical, a selectivity of \sim 40-50 is obtained. Here, a selectivity of > 200 was easily



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obtained. While these are very encouraging results but the control system is a critical factor to maintain the stability of the bath and selectivity over time. In IC manufacturing environment, the etch by-products saturate the process bath and suppress the SiO₂ etch and thus yielding inconsistent etch over time i.e. lower device yield. By monitoring the acids concentrations and refreshing the bath with fresh acids (sulfuric and phosphoric), this ensures that the bath has a low etch byproducts and thus consistent etch rate over time.

CONCLUSION

A process that utilizes a mix of sulfuric acid and phosphoric acid was developed. The process control also enabled us to extend the bath for many hours while achieving the same high ratio of silicon nitride to oxide etch rate.

REFERENCES:

Rotandaro, A.L.P., Hames, G.A., and Yocum, T, Electrochem. Soc. Proc. Vol. 99-36, pp. 385-390.

What is claimed is:

1. A method of etching silicon nitride from at least one substrate comprising:
supplying sulfuric acid, phosphoric acid, and water to a process chamber in
predetermined amounts so as to form a mixture having a predetermined concentration
ratio;

overflowing the process chamber with the mixture;
recirculating overflowed mixture back into the process chamber via a recirculation line;

submerging at least one substrate in the mixture within the process chamber; constantly monitoring the concentration ratio of the mixture with a concentration sensor;

upon the concentration sensor detecting the mixture having a concentration ratio other than the predetermined concentration ratio, automatically adding an amount of sulfuric acid, phosphoric acid, and/or water to the mixture to return the concentration ratio of the mixture back to or near the predetermined concentration ratio.

- 2. The method of claim 1 wherein the sulfuric acid, phosphoric acid, and water are initially supplied to the process chamber via dispense lines.
- 3. The method of claim 1 wherein the amount of sulfuric acid, phosphoric acid, and/or water added to the mixture to return the concentration ratio of the mixture to or near the predetermined concentration ratio are supplied via spike lines.
- 4. The method of claim 1 further comprising heating the mixture prior to submerging the at least one wafer therein.
- 5. The method of claim 4 wherein the mixture is heated to a temperature at or near 160-180°C.
- 5A. The method of claim 5 wherein the mixture is heated to a temperature at or near 165°C.
- 6. The method of claim 1 wherein the predetermined concentration ratio is approximately 2 parts sulfuric acid, 2 parts phosphoric acid, and 1 part water.
- 7. The method of claim 1 wherein the concentration sensor measures the concentration ration of the mixture along a recirculation line.
- 8. The method of claim 1 further comprising filtering the overflowed mixture.

9. The method of claim 1 further comprising:

bleeding a volume of mixture so as to reduce the effect of etch by products; and adding phosphoric acid, sulfuric acid, and/or water to replace the volume of mixture bled.

- 10. The method of claim 9 wherein a total volume of phosphoric acid, sulfuric acid, and/or water added to replace the bled mixture is approximately equal to the volume of the mixture drained.
- 11. The method of claim 9 wherein the mixture is bled at set intervals or continuously.
- 12. The method of claim 11 wherein the bleeding can be done while at least one substrate is submerged in the mixture or between batches of substrates.
- 13. A method of etching silicon nitride from at least one substrate comprising: supplying sulfuric acid, phosphoric acid, and water to a process chamber in predetermined amounts so as to form a predetermined volume of mixture having a predetermined concentration ratio;

circulating the mixture through the process chamber in a closed-loop system; submerging at least one substrate in the mixture within the process chamber; constantly monitoring the concentration ratio of the mixture with a concentration sensor;

bleeding a volume of mixture from the closed loop system so as to reduce the effect of etch by products in the circulating mixture; and

adding phosphoric acid, sulfuric acid, and/or water to replace the volume of mixture bled from the closed loop in amounts to maintain or return the concentration ratio of the mixture back to the predetermined concentration ratio.

- 14. The method of claim 13 wherein the bleeding is continuous or at set intervals.
- 15. The method of claim 13 further comprising upon the concentration sensor detecting the mixture having a concentration ratio other than the predetermined concentration ratio, automatically adding an amount of sulfuric acid, phosphoric acid, and/or water to the mixture to return the concentration ratio of the mixture back to or near the predetermined concentration ratio.
- 16. A system for etching silicon nitride from at least one substrate comprising: a process chamber;

means to supply sulfuric acid, phosphoric acid, and water to the process chamber in amounts so as to form a mixture having a predetermined concentration ratio;

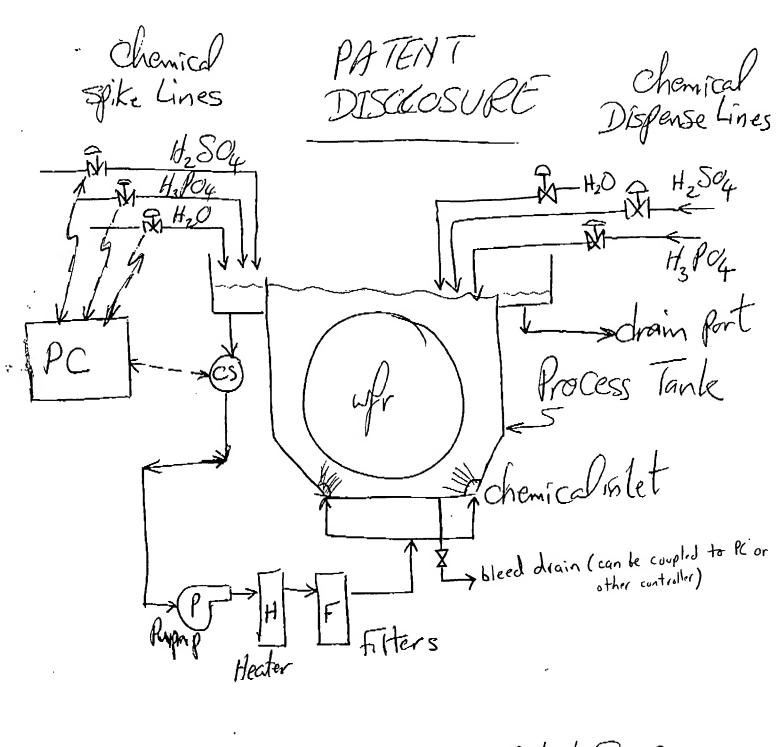
a recirculation line for circulating the mixture through the process chamber; means for adding sulfuric acid, phosphoric acid, and water to the mixture as necessary;

means to control fluid flow through the spike lines;

a concentration sensor that continuously measures the concentration ratio of the mixture and produces a signal indicative of the measured concentration ratio; and

a processor coupled to the concentration sensor for receiving the signal, the processor programmed so that upon receiving a signal indicative of a concentration ratio other than the predetermined concentration ratio, the processor automatically adds an amount of sulfuric acid, phosphoric acid, and/or water to the mixture necessary to return the concentration ratio of the mixture back to or near the predetermined concentration ratio.

- 17. The system of claim 16 wherein the process chamber comprises an overflow weir.
- 18. The system of claim 16 wherein the process chamber is adapted to receive a plurality of substrates.
- 19. The system of claim 16 further comprising a filter operably coupled to the recirculation line.
- 20. The system of claim 16 further comprising a heater coupled to the recirculation line and adapted to heat the mixture.
- 21. The system of claim 16 wherein the means to supply sulfuric acid, phosphoric acid, and water to the process chamber are a plurality of dispense lines with valves.
- 22. The system of claim 21 wherein the means to add sulfuric acid, phosphoric acid, and water to the mixture is a plurality of spike lines with valves.
- 23. The system of claim 16 further comprising a bleed drain for bleeding a volume of the mixture from the process chamber to reduce the effect of etch by products in the mixture.



CS: Chemical Concentration Control Sensor PC: Process Controller REST AVAILABLE COPY

Figure 1: Experimental Setup

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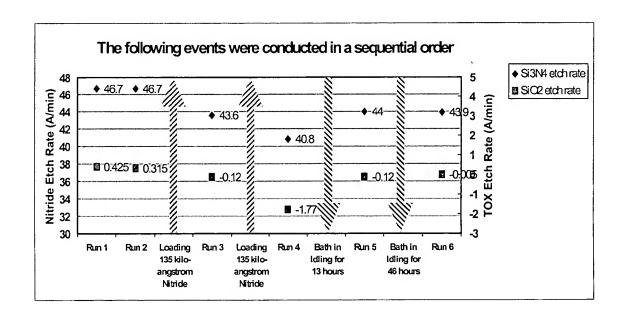
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Figure 2: Silicon Nitride to Silicon Dioxide etch over time.



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